(19) Japanese Patent Office (JP)
(12) **Kokai Unexamined Patent Application Bulletin (A)**

(11)	**Laid Open Patent Application No.**	2002-80647 (P2002-80647A)
(43)	**Publication Date**	March 19, 2002
	Number of Claims	4
	Number of Pages	6
	Examination Request	Not yet made

(51) Int. Cl.[7]	Identification Code	F1		Theme Code (ref.)
C 0 8 L 23/00		C 0 8 L 23/00		4 B 0 2 1
B 2 9 C 55/02		B 2 9 C 55/02		4 F 0 7 1
C 0 8 J 5/18	CES	C 0 8 J 5/18	CES	4 F 2 1 0
C 0 8 K 3/08		C 0 8 K 3/08		4 J 0 0 2
3/16		3/16		

Continued on the last page

(21) **Application No.:** 2000-271708(P2000-271708)

(22) **Application Date:** September 7, 2000

(71) **Applicant:** 000004466
Mitsubishi Gas Chemical Company, Inc.
2-5-2, Marunouchi, Chiyoda-ku, Tokyo

(72) **Inventor:** SAKAMOTO, Masaru
6-1-1, Shinjuku, Katsushika-ku, Tokyo
Mitsubishi Gas Chemical Company, Inc.
Tokyo Plant

(72) **Inventor:** NAGATA, Masateru
6-1-1, Shinjuku, Katsushika-ku, Tokyo
Mitsubishi Gas Chemical Company, Inc.
Tokyo Plant

(72) **Inventor:** HATAKEYAMA, Hidetoshi
6-1-1, Shinjuku, Katsushika-ku, Tokyo
Mitsubishi Gas Chemical Company, Inc.
Tokyo Plant

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(54) [Title of the Invention] Deoxygenation Agent Resin Composition and Sheet

(57) [Abstract]
[Means for Solving the Problems] A deoxygenation resin sheet that comprises a deoxygenation resin composition which is a resin composition comprising 15 to 75 parts by weight of polyolefin resin and 25 to 85 parts by weight of iron-based deoxygenation agent comprising iron, metal halide and inorganic sulfate, the inorganic sulfate being admixed to the iron-based deoxygenation agent at a weight ratio such that the weight of sulfur contained in the inorganic sulfate is 500 ppm to 5000 ppm with respect to the weight of the iron.
[Effect] Generation of hydrogen is limited and foodstuffs are optimally preserved without producing unpleasant odors or the like, by a deoxygenation sheet that prevents accidental ingestion as well as contamination of foodstuffs or the like which may result from powder leakage occurring with pouch-type deoxygenation agents.

[Claims]

[Claim 1] A deoxygenation resin composition which is a resin composition comprising 15 to 75 parts by weight of polyolefin resin and 25 to 85 parts by weight of iron-based deoxygenation agent comprising iron, a metal halide and an inorganic sulfate, said inorganic sulfate being admixed to said iron-based deoxygenation agent at a weight ratio such that the weight of sulfur contained in the inorganic sulfate is 500 ppm to 5000 ppm with respect to the weight of the iron.

[Claim 2] A deoxygenation resin sheet comprising the deoxygenation resin composition of Claim 1.

[Claim 3] A production method for deoxygenation resin sheets, characterized in that the deoxygenation resin composition of Claim 1 is melt-kneaded, extruded, and sheeted.

[Claim 4] A production method for deoxygenation resin sheets, characterized in that the deoxygenation resin composition of Claim 1 is melt-kneaded, extruded, and sheeted, and is then drawn.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention] The present invention relates to a deoxygenation composition used in deoxygenation sheets produced by kneading and sheeting a thermoplastic resin and an iron-based deoxygenation agent; and more specifically relates to a deoxygenation agent composition that is characterized by limiting hydrogen generation without generating unpleasant odors or tastes when used as a deoxygenation sheet formed by kneading and sheeting a thermoplastic resin and iron-based deoxygenation agent.

[0002]

[Prior Art] In the past, deoxygenation compositions produced by infusing an inorganic agent, activated charcoal or the like with an organic sodium ascorbate solution or the like, or deoxygenation compositions produced by blending an iron-based main component and, as necessary depending on the application, a promoter, were packaged in a packaging material that was partially or completely gas permeable, so as to produce a small pouch-form deoxygenation agent package, which was enclosed together with foodstuffs or the like in a packaging material having oxygen barrier properties, and these were used as deoxygenation agents with the aim of preserving the freshness of foods and the like.

[0003] Deoxygenation compositions that are packaged in deoxygenation packages are powdered or granular, and thus when a consumer accidentally damages the pouch for the deoxygenation agent with a cutting knife or the like, the deoxygenation agent composition is released from the pouch and there is the potential for contamination of the foodstuff that is stored. In addition, it is also possible for the body of the pouch-form deoxygenation agent to be cut as a result of maladjustment of the loading device during loading of the deoxygenation agent by the foodstuff manufacturer that is using the deoxygenation agent, when this is added to the foodstuff; and the deoxygenation agent composition thus can be released into the food packaging line and contaminate the foods.

[0004] A deoxygenation agent sheet and a mode for a deoxygenation agent produced using a sheet, directed at avoiding the risks associated with the powdered contents described above, were disclosed in JP-02-072851-A, JP-02-229840-A and the like, wherein the deoxygenation agent composition is kneaded in a thermoplastic resin. and extruded to form a sheet. Deoxygenation agent sheets in this series are vastly superior in terms of preventing powder leakage or accidental ingestion insofar as they resist release of the deoxygenation composition as compared to pouch-form deoxygenation agents that are produced by packaging powder-form deoxygenation agent compositions without modification.

[0005] Although deoxidization agents in which conventional deoxygenation resin compositions have been used have excellent capacities in terms of far superior resistance to powder leakage as described above, because resin and iron powder are kneaded in, odor is sometimes generated from the deoxidization resin composition, which degrades food quality or flavor. In order to inhibit odor, JP-02-298579-A describes the admixture of a deoxygenation agent with a copper content of 150 ppm or less and a sulfur content of 500 ppm or less to an ethylene-vinyl alcohol copolymer, and JP-10-230160-A describes various types of antioxidants that are admixed to resins.

[0006]

[Problems to Be Solved by the Invention] In the prior art described above, inhibition of odor generation by deoxygenation resin compositions is described, but it has been the case that hydrogen has been generated when deoxygenation resin compositions have been left in high-moisture atmospheres or when products that employ deoxygenation agent resin compositions have been used in foodstuffs with high water content or in medical products. When hydrogen generation is high, the foodstuff packaging bag used for the deoxygenation agent product can expand, which compromises the external appearance; or aggregate packaging bags for products that use deoxygenation resin compositions, which are normally in a degassed state, can swell, causing problems such as making it difficult to discern whether the outer bag has pinholes. An object of the present invention is to provide a deoxygenation agent resin composition that can effectively limit hydrogen generation while effectively limiting unpleasant odors generated by the deoxygenation resin composition.

[0007]

[Means for Solving the Problem] The inventors of the present invention discovered that a deoxygenation resin composition that can limit generation of hydrogen and generation of unpleasant odor by the deoxygenation agent resin composition can be provided by including an inorganic sulfate in the deoxygenation agent resin composition with a deoxygenation resin composition that is produced by blending and sheeting an iron-based deoxygenation agent with a thermoplastic resin.

[0008] The present invention is a deoxygenation resin composition which is a resin composition comprising 15 to 75 parts by weight of polyolefin resin and 25 to 85 parts by weight of iron-based dehydrogenation agent containing iron, a metal halide and an inorganic sulfate, the inorganic sulfate being admixed to the iron-based deoxygenation agent at a weight ratio such that the weight of the sulfur contained in the inorganic sulfate is 500 ppm to 5000 ppm with respect to the weight of iron. The present invention is also a deoxygenation sheet containing this deoxygenation resin composition and a method for production thereof.

[0009] JP-02-298579-A describes the admixture of a deoxygenation agent with a sulfur content of 500 ppm or less to an ethylene-vinyl alcohol copolymer, but the inventors of the present invention discovered that unpleasant odor is not generated and the production of hydrogen is limited by blending an inorganic sulfate with a resin composition containing polyolefin resin and iron-based deoxygenation agent in an amount such that the weight ratio of sulfur in the inorganic sulfate is 500 to 5000 ppm

with respect to the weight of iron in the iron-based deoxygenation agent.

[0010] Deoxygenation packages for medical products or foodstuffs that employ the deoxygenation resin composition of the present invention limit the amount of hydrogen generated during storage more than packages in which conventional deoxygenation resin compositions are used, and thus provide superior storage stability. In addition, it is also possible to provide superior stability in aggregate packages for products in which the deoxygenation resin composition is used.

[0011]

[Modes of Embodiment of the Invention] A specific constitution for the present invention is described below. The present invention is characterized in that an inorganic sulfate is contained in an iron-based deoxygenation resin composition, and the inorganic sulfate that is used is preferably used so that the sulfur content (S conversion) is 500 to 5000 ppm with respect to the weight of the iron in the iron-based deoxygenation agent composition. If the sulfur content of the inorganic sulfate is less than 500 ppm with respect to the iron, then the inhibitory effects of hydrogen generation will be poor, whereas if 5000 ppm is exceeded, stable production will not be possible because stable extrusion pressure will not be obtained during formation of a sheet from the deoxygenation resin composition, which is undesirable.

[0012] The iron-based deoxygenation agent composition has iron powder as its primary component, the promoter is a metal halide, and a composition is used to which an inorganic sulfate has also been added. There are no particular restrictions on the type of iron powder, and reduced iron powder, sprayed iron powder or electrolytic iron powder may be used. Ordinarily, the particle diameter is 200 μm or less, preferably 150 μm or less, in order to facilitate extrusion and drawing during sheet production. In addition, a metal halide such as sodium chloride, calcium chloride, iron chloride, magnesium chloride or another metal chloride, sodium bromide, potassium bromide, iron bromide or another metal bromide, or potassium iodide, calcium iodide or another metal iodide may be used as the promoter.

[0013] The metal halide promoter serves to increase the speed of the reaction between the iron and oxygen. The amount of the metal halide to be admixed is a weight ratio of 0.1 to 20 wt%, preferably 0.1 to 5 wt%, with respect to the iron in the deoxygenation agent composition. It is preferable for the surfaces of the iron powder to be coated with a metal halide salt, or for a metal halide salt to be dispersed and affixed thereto.

[0014] A water-soluble or water-insoluble inorganic sulfate is used as the inorganic sulfate, and specific examples include calcium sulfate, barium sulfate, magnesium sulfate, sodium sulfate, potassium sulfate, aluminum sulfate, ferrous sulfate or combinations thereof. The amount of inorganic sulfate admixed must be such that the weight ratio for the sulfur concentration in the inorganic sulfate is 500 to 5000 ppm with respect to iron in the deoxygenation agent composition. If the sulfur concentration in the inorganic sulfate is such that the sulfate concentration in the inorganic sulfate is less than 500 ppm with respect to the iron in the deoxygenation agent composition, then the hydrogen generation inhibitory effects will be poor; whereas if it is greater than 5000 ppm, then separation will be seen during kneading and extrusion with the thermoplastic resin, variation in extrusion pressure will occur, and continuous sheeting with high precision will be difficult, which is undesirable.

[0015] In order to improve dispersion, a material that has a particle diameter of 1/2 or less of the iron particles that are used, preferably 1/5 or less, is used as the blended inorganic sulfate. This iron powder-based deoxygenation agent composition may be a simple mixture of the above mentioned components, but is preferably a material produced by coating, or dispersing and affixing, the metal halide salt and inorganic sulfate onto the surface of the iron powder, or the mixture of the iron powder and activated charcoal or the like. Components such as activated charcoal and poorly water-soluble filler can also be added to this deoxygenation agent composition, as necessary.

[0016] There are no particular restrictions on the blending method for the inorganic sulfate, provided there is uniform dispersion in the deoxygenation resin composition or the deoxygenation sheet, and examples include the following types of methods. There is the sheeting method in which a promoter is applied after mixing the iron powder and inorganic sulfate, and after drying, extrusion and sheeting with the thermoplastic resin is carried out; the method wherein iron powder and promoter are coated or mixed, inorganic sulfate is mixed in, and when these have been uniformly dispersed, extrusion and sheeting are carried out together with the thermoplastic resin; or there is the method wherein iron powder and promoter are mixed, whereupon inorganic sulfate and thermoplastic resin are mixed, and extrusion and sheeting are carried out with deoxygenation composition containing the primary agent. In addition, [the inorganic sulfate] can be added by dispersion in the thermoplastic resin during sheet formation. In cases where coagulation occurs due to a reaction with water content, as in the case of calcium sulfate, or in cases where coagulation occurs as a result of combining the promoter and inorganic sulfate, it is preferable to select conditions such that mixing is carried out when [the components are] dry.

[0017] Examples of polyolefins to which the iron-based deoxygenation agent composition is admixed in the present invention include polyethylenes, as exemplified by low-density polyethylene, medium-density polyethylene, and linear low-density polyethylene and high-density polyethylene; polypropylenes, as exemplified by polypropylene homopolymer, propylene-ethylene block copolymer and propylene-ethylene random copolymer; polyolefins produced by metallocene catalysts such as metallocene polyethylene or metallocene polypropylene; and elastomers, as exemplified by polymethylpentene, ethylene-vinyl acetate copolymer and ethylene-α-olefin copolymer; or mixtures thereof. Among these, propylene-ethylene random copolymer, propylene-ethylene block copolymer, low-density polyethylene, linear low-density polyethylene or metallocene polyethylene are particularly preferred.

[0018] The deoxygenation resin composition of the present invention contains 15 to 75 parts by weight of polyolefin resin, 25 to 85 parts by weight of iron-based deoxygenation agent and the aforementioned amount of inorganic sulfate. The deoxygenation sheet can be readily produced, for example, by the method described in JP-02-072851-A. Specifically, iron powder-based deoxygenation agent is kneaded at a ratio of 25 to 85 parts by weight with respect to 15 to 75 parts by weight of the thermoplastic resin, and the material is fused, sheeted and drawn. The drawing ratio is preferably 150 to 1200%. The thickness of the deoxygenation sheet is preferably in the range of 0.2 to 3 mm, and appropriate selection is made in consideration of the required oxygen absorption capacity, processing properties, loading properties,

and the like.

[0019] The deoxygenation agent resin composition obtained in the present invention is normally used as a deoxygenation sheet that is covered, wholly or in part, with a gas-permeable packaging. Modes for the deoxygenation sheet are broadly classified into two modes: a mode in which a gas-permeable packaging material is used in order to package the deoxygenation sheet, and a sheathed mode in which a gas-permeable packaging material and the deoxygenation sheet are laminated. Specific examples of the deoxygenation sheet are presented in the following modes. However, the present invention is not restricted thereto.

[0020] 1) Mode in which the deoxygenation sheet is packed with gas-permeable packaging material

A mode in which the deoxygenation sheet is sandwiched between two packaging materials, with one surface being polyethylene terephthalate/polyethylene and the other surface being water-resistant non-woven cloth (e.g.,"Tyvek" manufactured by DuPont, or "Luxar", manufactured by Asahi Kasei Kogyo), and the periphery thereof is heat- sealed.

[0021] 2) Label-type mode in which the deoxygenation sheet, gas permeable packaging material and adhesive material are combined

A label-type mode wherein, for example, a base layer having an adhesive layer, the deoxygenation sheet, and a gas-permeable layer are laminated in sequence, and the gas-permeable layer is bonded directly to the base layer at the periphery; or a label-type mode with an integrated display label wherein a gas-permeable adhesive layer, gas-permeable packaging material layer, the deoxygenation sheet, an adhesive layer, and a display label layer are laminated in sequence.

[0022] 3) Mounting paper mode in which the deoxygenation sheet is laminated with, or enclosed in, a gas-permeable packaging material

A conventional packaging material for deoxygenation agent packages can be used as the gas-permeable packaging material. Examples include packaging materials produced by lamination of porous film to paper, and packaging materials produced by laminating porous film to water-resistant nonwoven cloths (e.g., "Tyvek", manufactured by DuPont, or "Luxar", manufactured by Asahi Kasei Kogyo), various types of microporous films (e.g., "Duraguard", manufactured by Celanese, "NF Sheet", manufactured by Tokuyama Soda, or "Nitoflon", manufactured by Nitto Denko), the water-resistant nonwoven cloth or microporous film described above, as well as materials produced by subjecting these materials to water resistance and oil resistance treatments.

[0023]

[Working Examples] A more detailed description is presented below using working examples, but the present invention is not restricted to these working examples.

[0024] Working Example 1

Production of deoxygenation sheet: Barium sulfate in the amount of 0.5 parts by weight was added and mixed with respect to 100 parts by weight of iron powder (average particle diameter 70 μm), whereupon a solution of 2 parts by weight of calcium chloride dissolved in 2 parts by weight of water was sprayed and mixed, and an iron-based deoxygenation agent composition was obtained by drying in hot hair. The iron-based deoxygenation agent composition in the amount of 100 parts by weight and 40 parts by weight of high-density polyethylene were mixed, and were then heated and melted at 190°C, and filmed into the form of a sheet with an extruder. This sheet was drawn 800% in the longitudinal direction at 110°C to produce a deoxygenation sheet with a thickness of 0.5 mm.

Production of deoxygenation package: The resulting deoxygenation sheet was cut to a size of 30 mm x 30 mm, one surface was covered with 50 x 50 mm polyethylene terephthalate/polyethylene film packaging material, the other surface was covered with a 50 x 50 mm water-resistant nonwoven cloth packaging material ("Tyvek", manufactured by DuPont), and the four edges were heat-sealed at a width of 5 mm each to produce a card-form deoxygenation resin package.

[0025] The deoxygenation sheet package that had been produced and absorbent cotton containing 5 mL of water were sealed together with 25 mL of air in a gas barrier bag composed of aluminum/nylon/polyethylene laminate film, and the hydrogen and oxygen concentrations in the bag were measured after storing for 3 days at 35°C.

[0026] Working Example 2

Production of deoxygenation sheet: A solution of 2 parts by weight of calcium chloride dissolved in 2 parts by weight of water was sprayed and mixed with 100 parts by weight of iron powder (average particle diameter 70 μm), and after drying with hot air, 2.5 parts by weight of anhydrous calcium sulfate was added and mixed to obtain an iron-based deoxygenation agent composition. The iron-based deoxygenation agent composition in the amount of 100 parts by weight and 40 parts by weight of high-density polyethylene were mixed, heated and fused at 190°C, and filmed in the form of a sheet using an extruder. This sheet was drawn at 800% in the longitudinal direction at 110°C to produce a deoxygenation sheet with a thickness of 0.5 mm, and with this exception, processing was carried out in the same mode as in Working Example 1 to produce a card-form deoxygenation resin package. The resulting card-form deoxygenation resin package and absorbent cotton containing 5 mL of water were sealed together with 100 mL of air in a gas barrier bag, and the hydrogen and oxygen concentrations were measured after storing for 90 days at 25°C, whereupon the bag was opened and checked for unpleasant odor.

[0027] Working Example 3

Production of deoxygenation sheet: A solution of 1 part by weight of sodium chloride and 1 part by weight of sodium sulfate dissolved in 4 parts by weight of warm water was sprayed and mixed with 100 parts by weight of iron powder (average particle diameter 50 μm), and an iron-based deoxygenation agent composition was obtained by drying with hot air. The iron-based deoxygenation agent composition in the amount of 60 parts by weight and 40 parts by weight of linear low-density polyethylene were mixed, heated and fused at 150°C, and then filmed into the form of a sheet using an extruder. This sheet was drawn at 600% in the longitudinal direction at 95°C to produce an oxygen deoxygenation sheet [*sic*] with a thickness of 0.5 mm, and with this exception, processing was carried out in the same mode as in Working Example 1 to produce a card-form deoxygenation resin package. The resulting card-form deoxygenation resin package and absorbent cotton containing 5 mL of water were sealed together with 100 mL of air in a gas barrier bag, and the hydrogen and oxygen concentrations were measured after storing for 10 days at 30°C, whereupon the bag was opened and checked for unpleasant odor.

[0028] Comparative Example 1

Production of deoxygenation sheet: A solution of 2 parts by weight of calcium chloride dissolved in 2 parts by weight of water was sprayed and coated onto 100 parts by weight of iron powder (average particle diameter 70 μm), and an iron-based deoxygenation agent composition was obtained by drying with hot air. The iron-based deoxygenation agent in the amount of 100 parts by weight and 40 parts by weight of high-density polyethylene were mixed, heated and fused at 190°C, and then filmed into the form of a sheet using an extruder. This sheet was drawn at 800% in the longitudinal direction at 110°C to produce an oxygen deoxygenation sheet [*sic*] with a thickness of 0.5 mm; and with this exception, processing was carried out in the same mode as in Working Example 1; and the resulting card-form deoxygenation resin package was used in order to check hydrogen and odor generation under the same conditions.

[0029] Comparative Example 2

Production of deoxygenation sheet: A solution of 2 parts by weight of calcium chloride dissolved in 2 parts by weight of water was sprayed and mixed with a material produced by adding and mixing 700 ppm of powdered sulfur with 100 parts by weight of iron powder (average particle diameter 70 μm), and an iron-based deoxygenation agent composition was obtained by drying with hot air. The iron-based deoxygenation agent composition in the amount of 100 parts by weight and 40 parts by weight of high-density polyethylene were mixed, heated and fused at 190°C, and then filmed into the form of a sheet using an extruder. This sheet was drawn at 800% in the longitudinal direction at 110°C to produce an oxygen deoxygenation sheet [*sic*] with a thickness of 0.5 mm; and, with this exception, processing was carried out in the same mode as in Working Example 1; and the resulting card-form deoxygenation resin package was used in order to check hydrogen and odor generation under the same conditions.

[0030] Comparative Example 3

Production of deoxygenation sheet: A solution of 2 parts by weight of calcium chloride dissolved in 2 parts by weight of water was sprayed and mixed with 100 parts by weight of iron powder (average particle diameter 70 μm), and after drying with hot air, 5 parts by weight of barium sulfate was added and mixed to obtain an iron-based deoxygenation agent composition. The iron-based deoxygenation agent composition in the amount of 100 parts by weight and 40 parts by weight of high-density polyethylene were mixed, and were then heated and fused at 190°C, but when an attempt was made to film the material into the form of a sheet using an extruder, stable extrusion pressure was not obtained, and continuous filming could not be stably carried out.

[0031]

[Table 1]

Table: Results from the working examples and comparative examples

	Sulfur content (ppm)[1]	Hydrogen concentration (%)	Oxygen concentration (%)	Odor evaluation [2]	Sheet production
Working Example 1	686	4.86	0.1 or less	0	No problems
Working Example 2	4646	4.41	0.1 or less	0	No problems
Working Example 3	2253	4.50	0.1 or less	0	No problems
Comparative Example 1	0	19.83	0.1 or less	0	No problems
Comparative Example 2	0	3.80	0.1 or less	3	No problems
Comparative Example 3	6855	-	-	-	Stable filming not possible

(1) Weight of sulfur in inorganic sulfate with respect to weight of iron in iron-based deoxygenation agent.

(2) Odor evaluation

0: No odor detected

1: Slight odor detected

2: Unpleasant odor

3: Strong unpleasant odor

[0032]

[Effect of the invention] With the deoxygenation resin composition of the present invention, generation of hydrogen is limited and no unpleasant odor is generated due to the addition of iron-based deoxygenation agent containing a certain amount of inorganic sulfate. Deoxygenation sheets can be produced from the deoxygenation resin composition of the present invention without problems. The deoxygenation sheet of the present invention is thus desirable for use in foodstuff storage, because it limits the generation of hydrogen, without generating odor.

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(51) Int. Cl.[7]	Identification Code	F1		Theme Code (ref.)
C 0 8 K 3/30		C 0 8 K 3/30		
// A 2 3 L 3/3436	501	A 2 3 L 3/3436	501	
B 2 9 K 23:00		B 2 9 K 23:00		
B 2 9 L 7:00		B 2 9 L 7:00		

F Term (ref.)	4B021	LA17 MC04 MK08 MK09 MK14 MP05
	4F071	AA14 AA16 AB08 AB13 AB24 AD06 AE22 AF01 AF03 AF52 AH04 BB06 BB07 BC01 BC12
	4F210	AA03 AA05 AB01 AB16 AG01 QC02 QG01 QG11 QG18
	4J002	BB031 BB051 BB061 BB121 BB151 BB171 BP021 DA086 DD057 DD067 DD077 DD087 DG047 DG057 GG02